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(54) **HEXAHYDROTRIAZINE, DITHIAZINE, AND THIOETHER FUNCTIONALIZED MATERIALS**

(56) **References Cited**

U.S. PATENT DOCUMENTS

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2,889,277 A	6/1959	Hughes
3,340,232 A	9/1967	Smith et al.
3,598,748 A	8/1971	Hirosawa
3,957,742 A	5/1976	Kveton
4,106,904 A	8/1978	Oude Alink et al.
4,224,417 A	9/1980	Hajek et al.
4,225,481 A	9/1980	Wagner

(Continued)

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FOREIGN PATENT DOCUMENTS

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CN	101265255 A	9/2008
EP	2636697 A1	9/2013

(Continued)

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OTHER PUBLICATIONS

Appendix P; List of IBM Patents or Patent Applications Treated as Related.

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Primary Examiner — Shane Fang

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C08F 12/28 (2006.01)
C08F 12/30 (2006.01)

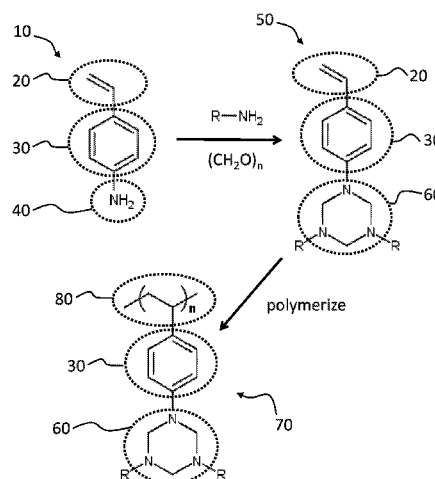
(52) **U.S. Cl.**
CPC **C08F 12/28** (2013.01); **C08F 12/30** (2013.01)

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CPC H01L 51/0067; H01L 51/0072
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See application file for complete search history.

ABSTRACT

Synthetic schemes for preparation of polymers and polymer precursors having various functional groups is provided. These synthetic schemes are used to prepare polymeric, oligomeric, or monomeric materials incorporating 1,3,5-hexahydrotriazine moieties. These hexahydrotriazine moieties can be further reacted to form dithiazine and thioether moieties. In certain synthetic schemes, 1,3,5-hexahydrotriazine moieties are incorporated as crosslinker groups for providing crosslinked polymeric materials. Crosslinker groups formed with these triazine moieties provide chemically reversible crosslinks, which allow such otherwise intractable crosslinked polymeric materials to be recycled and/or reprocessed by removal/reversal of crosslinks.

17 Claims, 7 Drawing Sheets



(56)

References Cited

U.S. PATENT DOCUMENTS

4,246,160	A	1/1981	Wagner et al.	
4,301,262	A	11/1981	Wagner et al.	
4,310,633	A *	1/1982	Haas et al.	521/129
4,877,451	A	10/1989	Winnik et al.	
5,112,796	A	5/1992	Iannicelli	
5,674,377	A	10/1997	Sullivan, III et al.	
5,830,243	A	11/1998	Wolak et al.	
7,384,434	B2	6/2008	Malfer et al.	
2010/0107476	A1	5/2010	Cosimbescu	
2012/0049308	A1	3/2012	Nishimura et al.	

FOREIGN PATENT DOCUMENTS

GB	928112	A	6/1963
GB	1531578	A	11/1978
WO	0166614	A2	9/2001
WO	0198388	A1	12/2001
WO	0226849	A1	4/2002

OTHER PUBLICATIONS

Henri Ulrich et al., Reaction of Chloromethyl Ether with Primary Amines, May 1961, pp. 1637-1638.

Hemant S. Patel et al., Studies on Synthesis and Characterization of some Novel Aromatic Copolyesters based on s-Triazine, Iranian Polymer Journal, vol. 14, No. 12, 2005, pp. 1090-1098.

Fabian Suriano et al., Functionalized cyclic carbonates: from synthesis and metal-free catalyzed ring-opening polymerization to applications, Polymer Chemistry, The Royal Society of Chemistry, 2011, Received Jul. 6, 2010, Accepted Aug. 13, 2010, pp. 528-533.

Wang Yulan et al., Synthesis and Properties of Poly-1, 3, 5-Triazines, Polymer Communications, No. 2, 1984, pp. 117-123.

John Markoff, Error at IBM Lab Finds New Family of Materials, New York Times, May 15, 2014, 4 pages.

Jeanette M. Garcia et al., Recyclable, Strong Thermosets and Organogels via Paraformaldehyde Condensation with Diamines, Science AAAS, vol. 344, May 16, 2014, pp. 732-735.

D.R. Anderson et al., Thermally resistance polymers containing the s-triazine ring, Journal of Polymer Science Part A-1: Polymer Chemistry, vol. 4, Issue 7, pp. 1689-1702.

T. Okita, Filter method for the determination of trace quantities of amines, mercaptans, and organic sulphides in the atmosphere, Atmospheric Environment (1967), vol. 4, Issue 1, Jan. 1970, pp. 93-102.

Raquel Lebrero et al., Odor abatement in biotrickling filters: Effect of the EBRT on methyl mercaptan and hydrophobic VOCs removal, Bioresource Technology, Special Issue: Innovative Researches on Algal Biomass, vol. 109, Apr. 2012, pp. 38-45.

Elbert, et al. "Conjugate Addition Reactions Combined with Free-Radical Cross-Linking for the Design of Materials for Tissue Engineering," Biomacromolecules 2001, 2, 430-441; Published on Web Mar. 3, 2001.

Ferrari, "Reactions of Formaldehyde With Aromatic Amines," J. Appl. Chem, 14, 1964, 389-399.

Geng, et al., "Nanoindentation behavior of ultrathin polymeric films," Polymer 46 (2005) 11768-11772; Available online Oct. 19, 2005.

Hiller, et al., "Laser-engrivable hexahydrotriazine polymer networks," Mat Res Innovat (2002) 6:179-184.

Oliver, et al. "Measurement of hardness and elastic modulus by; instrumented indentation: Advances in understanding and; refinements to methodology," J. Mater. Res., vol. 19, No. 1, Jan. 2004, 3-20.

Singh, et al., "Ultrasound mediated Green Synthesis of Hexa-hydro Triazines," J. Mater. Environ. Sci. 2 (4) (2011) 403-406.

Stafford, et al., "A buckling-based metrology for measuring; the elastic moduli of polymeric thin films," Nature Materials Aug. 3, 2004, 545-550; Published online: Jul. 11, 2004.

U.S. Appl. No. 14/510,477, entitled Hexahydrotriazine, Dithiazine, and Thioether Functionalized Materials, filed Oct. 9, 2014.

Appendix P: List of IBM Patents or Patent Applications Treated as Related, Dec. 2014.

* cited by examiner

FIG. 1

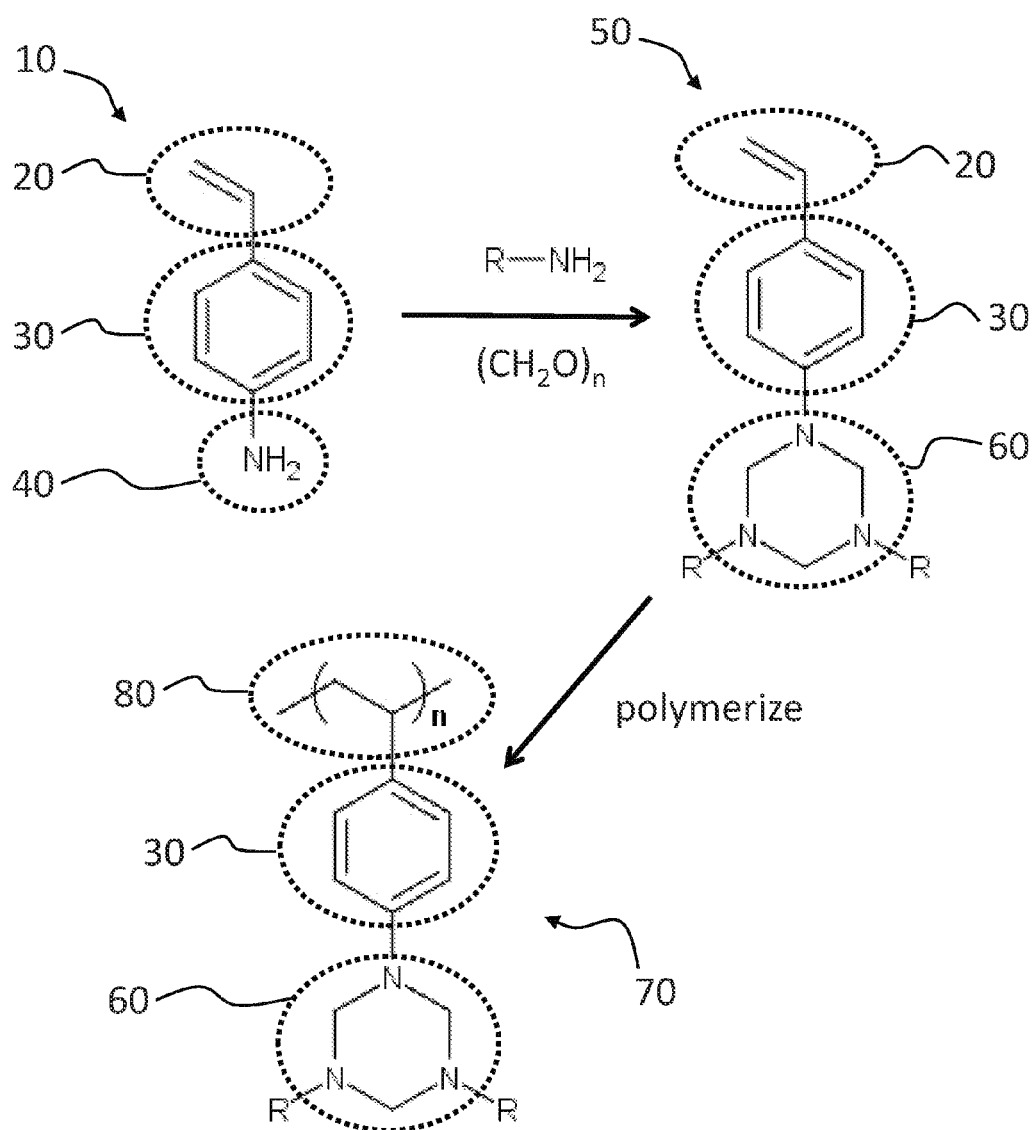


FIG. 2

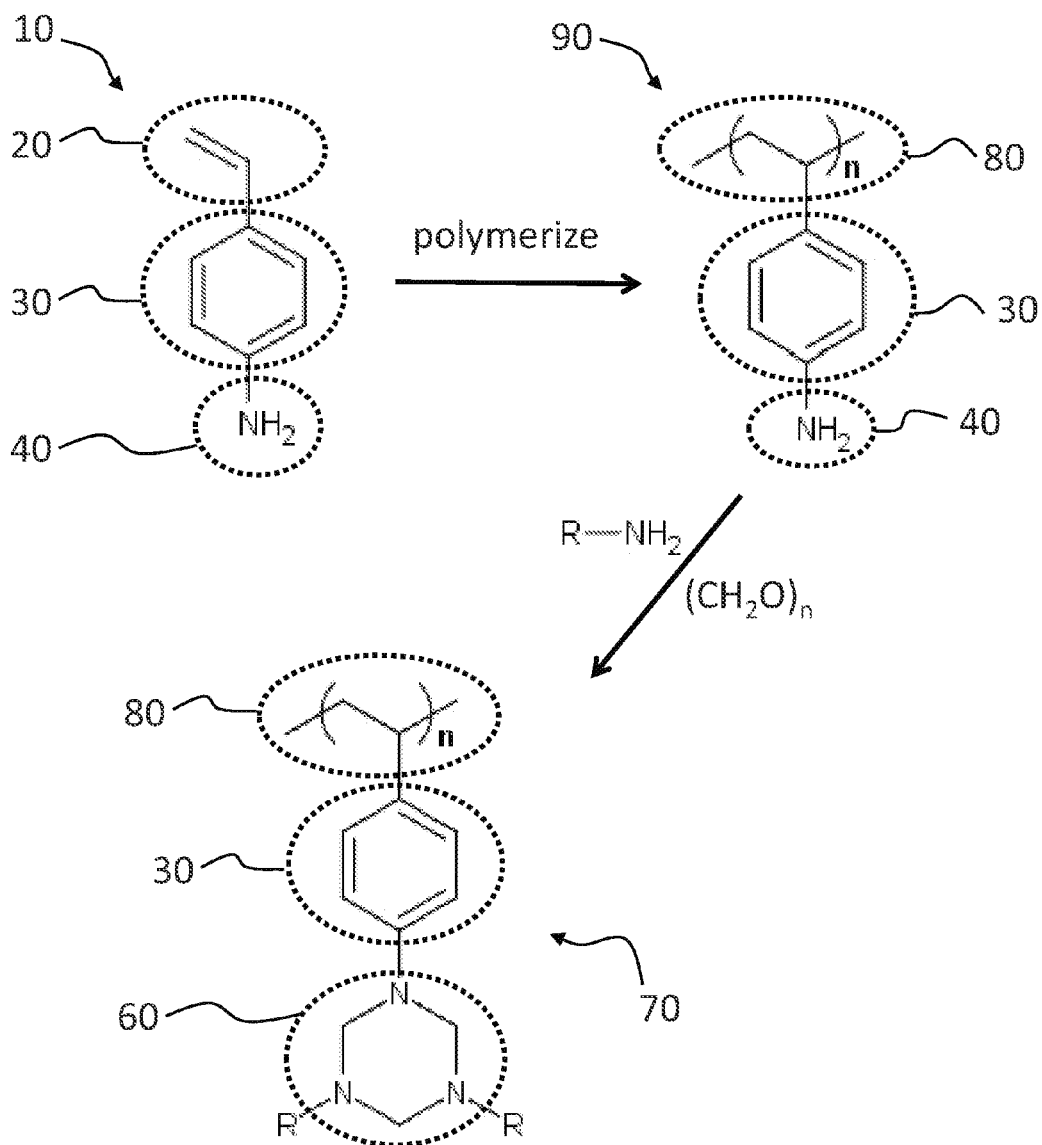


FIG. 3

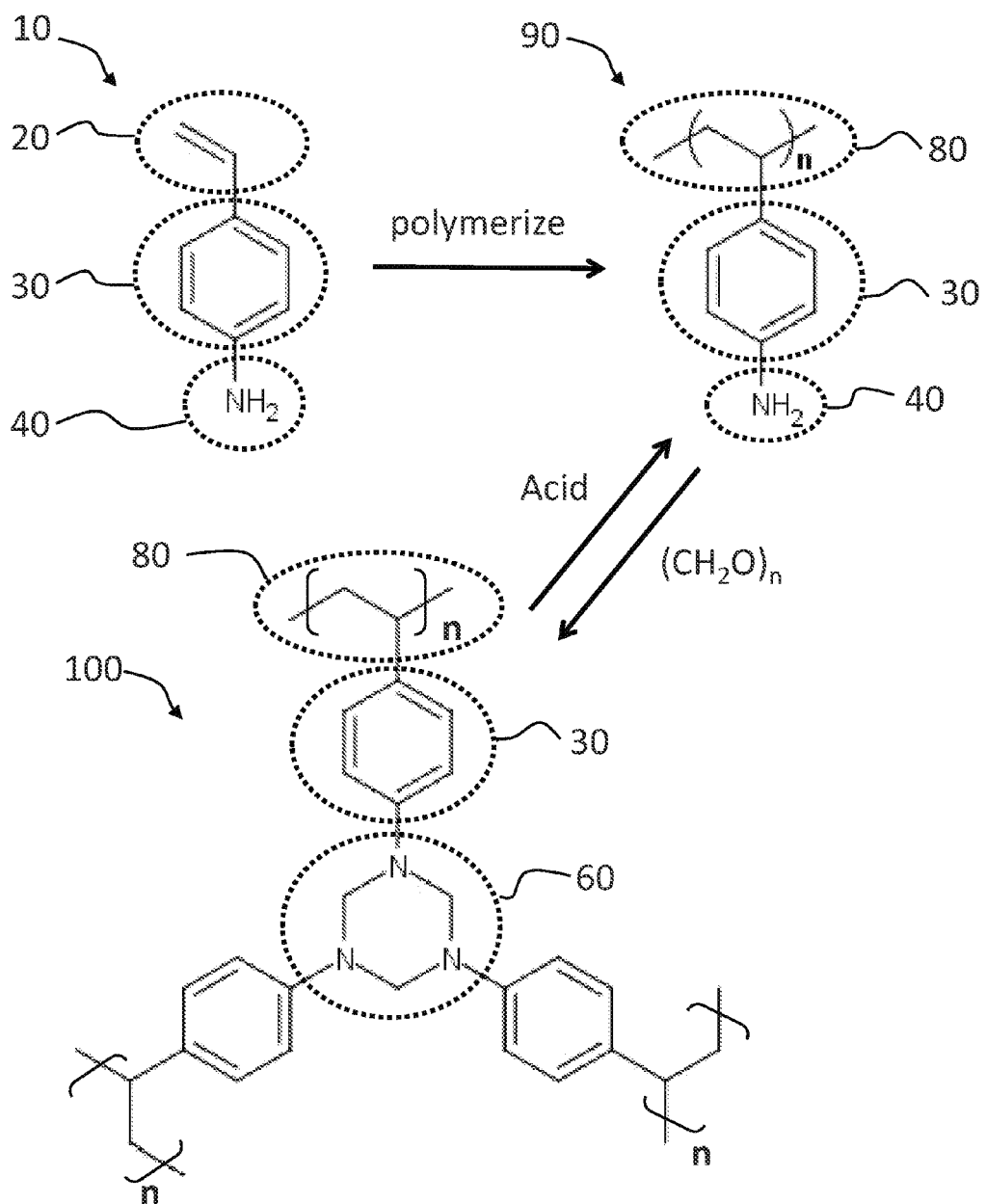
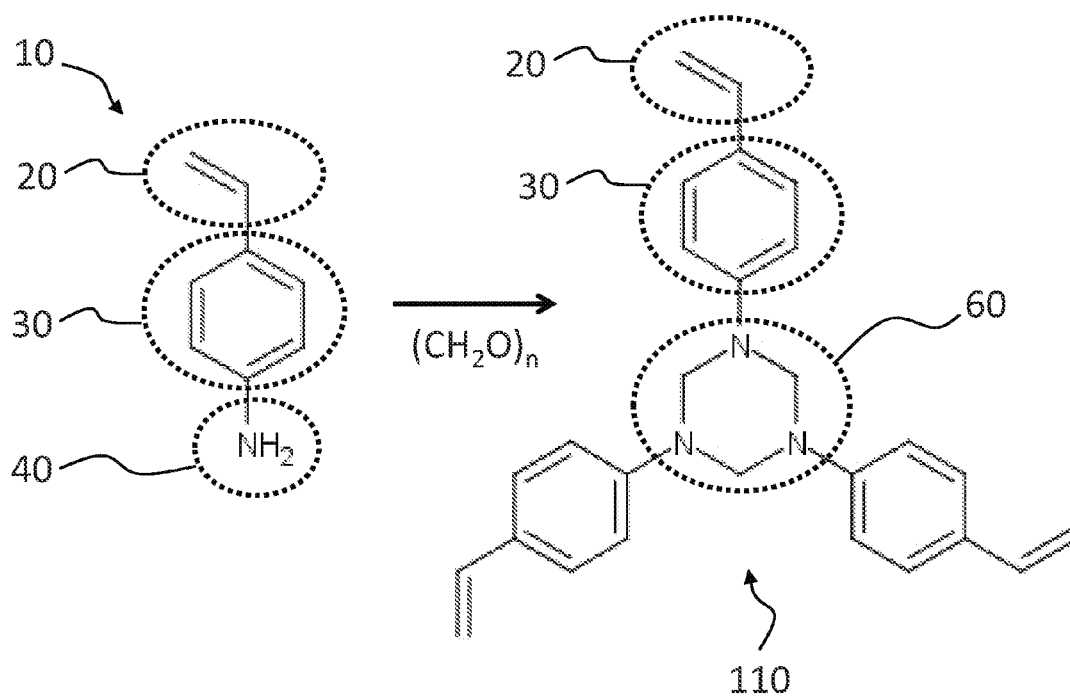


FIG. 4



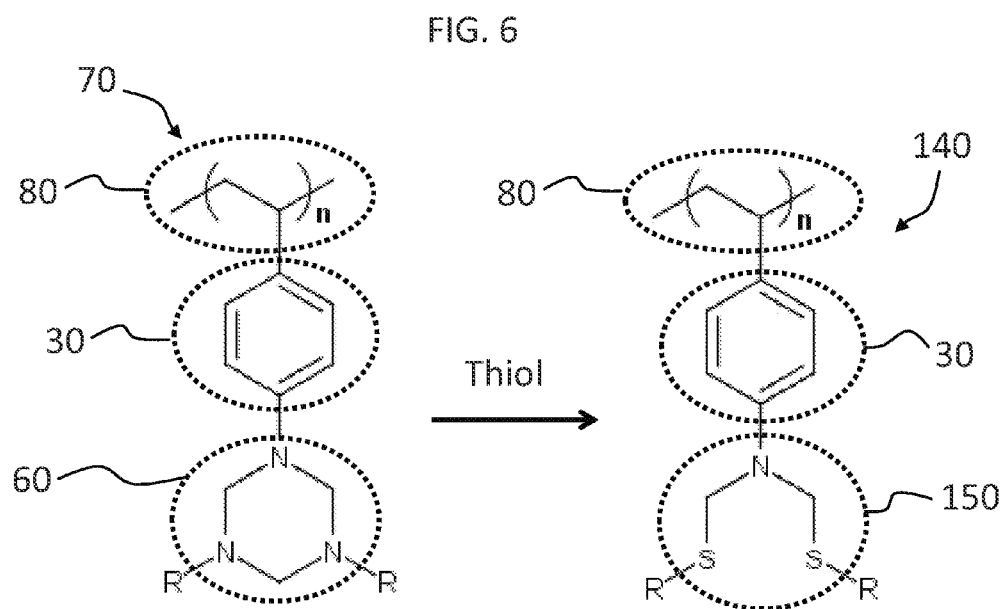
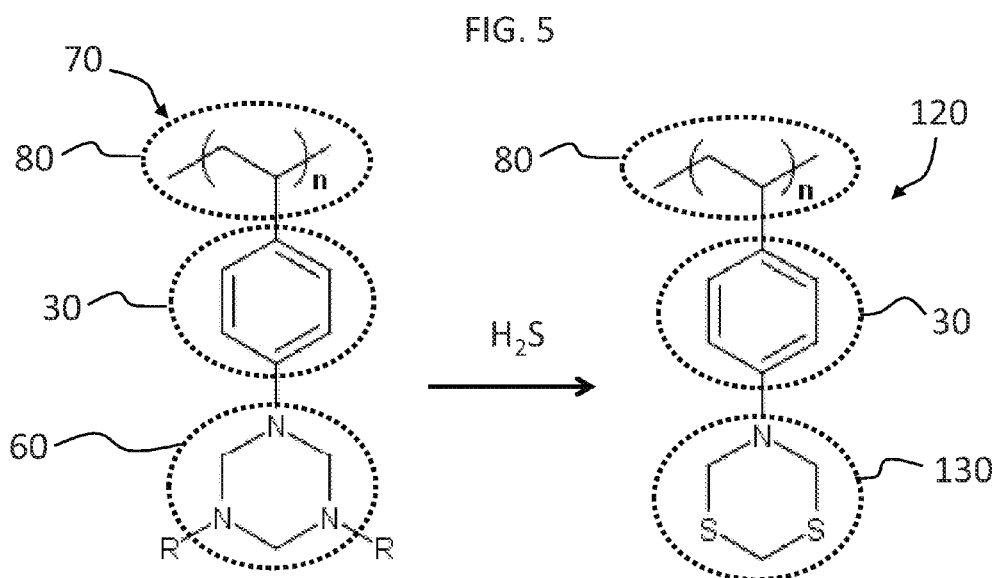


FIG. 7

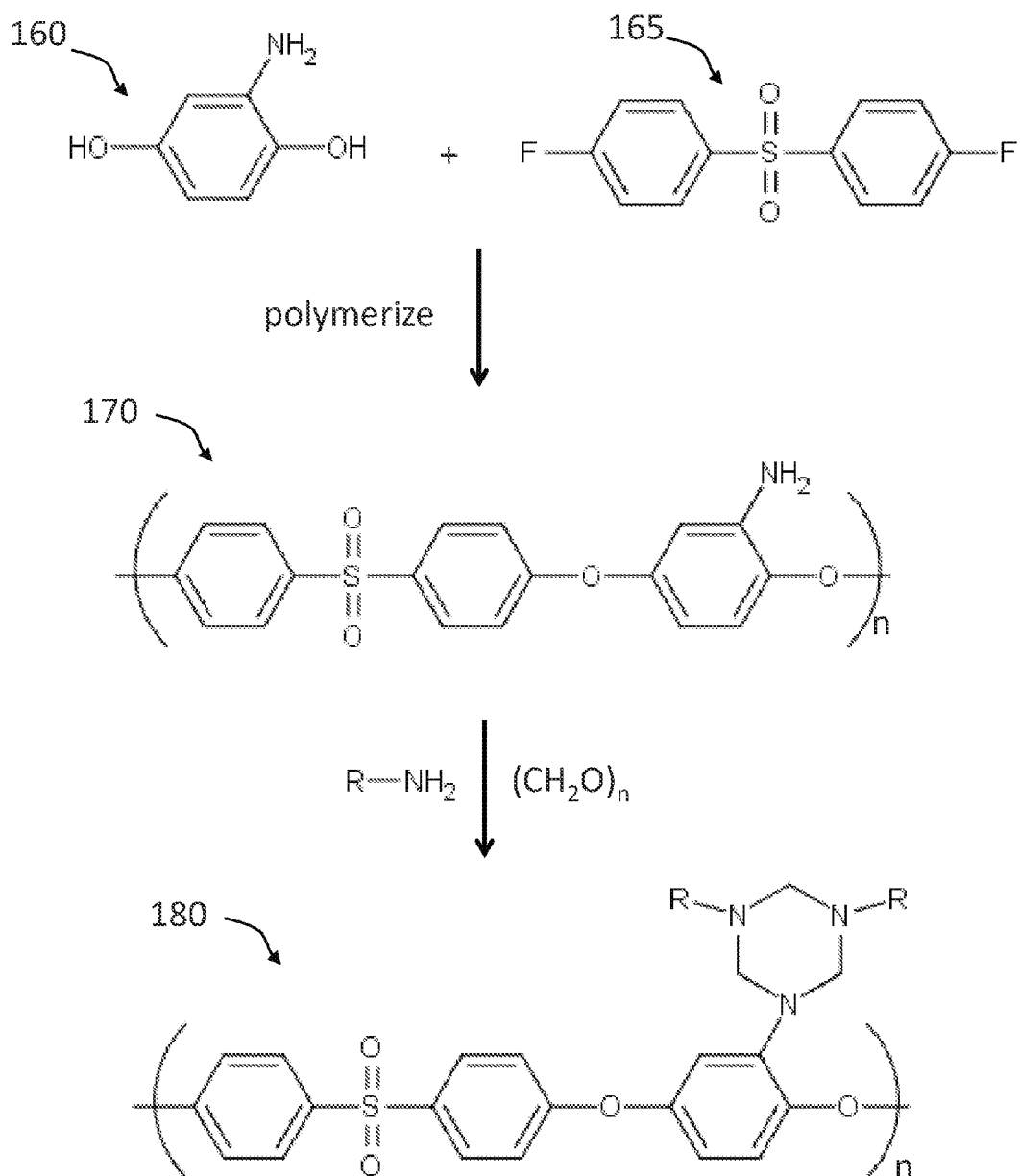
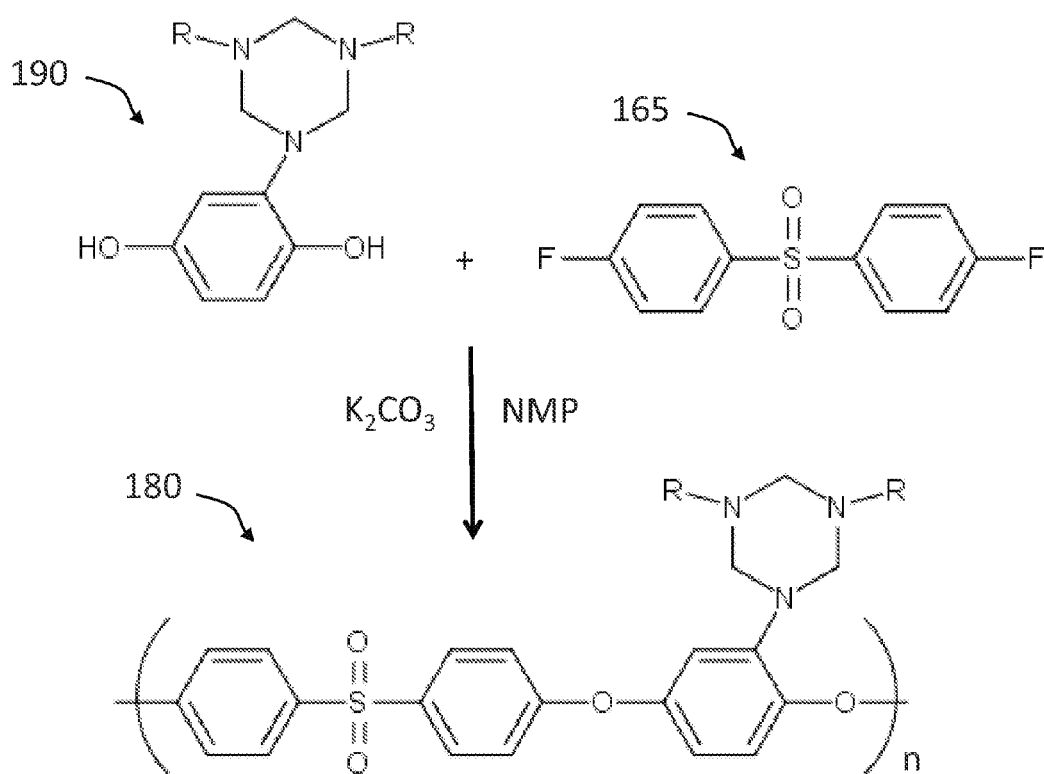


FIG. 8



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HEXAHYDROTRIAZINE, DITHIAZINE, AND THIOETHER FUNCTIONALIZED MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of co-pending U.S. patent application Ser. No. 14/510,477, filed Oct. 9, 2014. The aforementioned related patent application is herein incorporated by reference in its entirety.

INCORPORATION BY REFERENCE

Various example polyhexahydrotriazine and polyhemiaminal materials and synthetic details related thereto are provided in commonly assigned, co-pending application Ser. No. 14/050,995, filed in the USPTO on Oct. 10, 2013, the entirety of which is incorporated herein by reference.

BACKGROUND

The present disclosure relates to functionalized materials and more specifically to triazine, dithiazine, and thioether functionalized materials.

Synthesis of polyhexahydrotriazines (PHT) and polyhemiaminal (PHA) by the reaction of aromatic diamines and paraformaldehyde has been disclosed. These PHT and PHA materials have many desirable properties and potential uses. For example, PHT resins can be recycled to starting materials upon exposure to strong acids even though the PHT resins are initially highly crosslinked. PHT and PHA materials can also be used to scavenge hydrogen sulfide and will react with thiols to produce thioether polymers. It would, in general, be desirable to incorporate features of PHT and PHA materials into other materials.

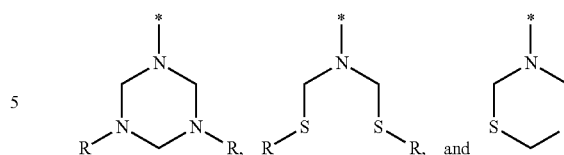
SUMMARY

According to one embodiment of the present disclosure, a method includes exposing a first monomer including a primary amine functional group to paraformaldehyde and a first primary amine compound ($R-NH_2$). Reaction between the primary amine group on the first monomer with the paraformaldehyde and the first primary amine compound forms a second monomer including a 1,3,5-hexahydrotriazine group. The second monomer can then be polymerized. A first polymer including the 1,3,5-hexahydrotriazine group can be thus be formed using the second monomer. In an optional step, the first polymer can be exposed to hydrogen sulfide to form a dithiazine functionality. In a different optional step, the first polymer can be exposed to a thiol compound to form a thioether functionality.

According to another embodiment, a method includes polymerizing a first monomer having a primary amine functional group and forming a first polymer including the primary amine functional group. The first polymer is then exposed to paraformaldehyde and a first primary amine compound ($R-NH_2$) and a second polymer including a 1,3,5-hexahydrotriazine group is formed. In some embodiments, the first primary amine compound can have the same chemical structure as the first polymer and/or may be a portion of the first polymer.

According to still another embodiment, a polymer includes a first polymeric repeat unit with a first pendant group having a structure selected from:

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wherein each R group represents a radical unit including at least one carbon and each starred (*) bond represents a point of attachment to the first polymeric repeat unit.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts an exemplary synthetic scheme for preparing a 1,3,5-hexahydrotriazine functionalized monomer and a 1,3,5-hexahydrotriazine functionalized polymer

FIG. 2 depicts an exemplary synthetic scheme for preparing a 1,3,5-hexahydrotriazine functionalized polymer.

FIG. 3 depicts an exemplary synthetic scheme for preparing a chemically reversing crosslinked polymer material.

FIG. 4 depicts an exemplary synthetic scheme for preparing a chemically reversing crosslinkable monomer material.

FIG. 5 depicts an exemplary synthetic scheme for preparing a dithiazine functionalized polymer.

FIG. 6 depicts an exemplary synthetic scheme for preparing a thioether functionalized polymer.

FIG. 7 depicts an exemplary synthetic scheme for preparing a 1,3,5-hexahydrotriazine functionalized polymer from an amino-substituted aromatic diol-type monomer.

FIG. 8 depicts an exemplary synthetic scheme for preparing a 1,3,5-hexahydrotriazine functionalized polymer from a 1,3,5-hexahydrotriazine-substituted aromatic diol-type monomer.

DETAILED DESCRIPTION

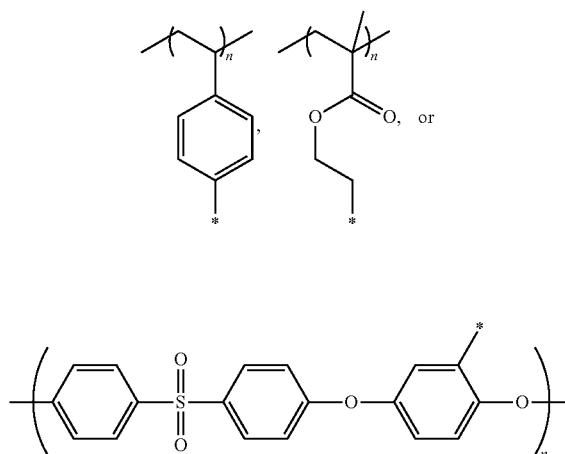
In general, a series of example synthetic schemes for preparation of polymers and polymer precursors having various functional groups is provided. These synthetic schemes are used to prepare polymeric, oligomeric, or monomeric materials incorporating 1,3,5-hexahydrotriazine moieties. These 1,3,5-hexahydrotriazine moieties can be further reacted to form dithiazine and thioether moieties. In certain synthetic schemes, 1,3,5-hexahydrotriazine moieties are incorporated as crosslinker groups for providing crosslinked polymeric materials. Crosslinker groups formed with hexahydrotriazine moieties provide chemically reversible crosslinks, which allow such otherwise intractable crosslinked polymeric materials to be recycled and/or reprocessed by removal/reversal of crosslinks.

Polymeric materials prepared according to the example schemes correspond to following structure:

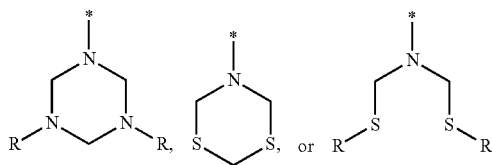
BB—PG

where BB is a polymeric or oligomeric group. In some embodiments, BB has a structure incorporating at least one of the following chemical structures:

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and PG has a chemical structure corresponding to one of the following:



where "R" corresponds to a radical unit including at least one carbon atom. "R" may be the same or different in each instance of use within the depicted chemical structures. That is, two or more "R" groups depicted in a single chemical structure are not necessarily the same radical unit, though they may be the same in some embodiments. Without limitation, a radical unit depicted as "R" may include an alkyl group, an aryl group, a silane group, an alkyne group, an alkene group, an alcohol group, an epoxide group, an amine group, a cyanate group, a carboxylic acid group, an ester group, a phenolic group, and/or a succinimide group. In specific embodiments, the radical unit depicted as "R" may be a methyl group, a methanol group, a primary amine substituted alkyl group, a tertiary amine substituted alkyl group, or a triethoxysilane group. "R" may also represent a portion of polymeric or oligomeric chain having a structure corresponding to the depicted BB. The starred (*) bond of the depicted BB and PG groups represent points of linkage between the BB and PG groups—that is, the starred (*) bond in the BB group is directly linked to the starred (*) bond in the PG group.

Certain example synthetic schemes of the present disclosure depict preparation and/or use of poly(4-aminostyrene) precursors, poly(4-aminostyrene) intermediates, and poly(4-aminostyrene) derivatives. However, these examples are for purposes of explanation of various aspects of the present disclosure and should not be considered limiting. Other polymeric, oligomeric, and monomeric materials, precursors, intermediates, and derivatives may be prepared and/or used according to the present disclosure. For example, 1,3,5-hexahydrotriazine moieties in monomeric, oligomeric, and polymeric materials can also be formed using amino-functionalized methacrylate materials, such as 2-amino-ethyl methacrylate, as starting material. Additionally, amino-functionalized polyaromatic carbonates, aliphatic polycarbon-

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ates, and poly(aryl ethers) can be used as starting materials for formation of 1,3,5-hexahydrotriazine moieties according to the present disclosure. In some embodiments, the starting material may be an amino-functionalized diol-type monomer such as 2-aminobenzene-1,4-diol or an amino-functionalized bisphenol-type monomer such as 2-amino-4-(3-amino-4-hydroxyphenyl)phenol or 2-amino-4-[2-(3-amino-4-hydroxyphenyl)propan-2-yl]phenol that may be polymerized in step-growth polymerizations or condensation-type polymerizations. In some embodiments, the monomer used as a starting material may be one of an amino-substituted styrene, an amino-substituted bisphenol, an amino-substituted aromatic diol, and an amino-substituted methacrylate. In this context, "poly(aryl ethers)" are polymers including aromatic (e.g., phenylene) and ether-type (—O—) linkages in the BB group.

In general, the BB group may be formed by any polymer-forming reaction in which a primary amine moiety can be a spectator—that is, uninvolved (or substantially uninvolved) in the polymerization reaction. Polymerization methods for forming the BB group include chain-growth polymerizations (e.g., free radical type polymerizations) and step-growth polymerizations (e.g., condensation polymerizations or addition polymerizations). In a particular example, nucleophilic aromatic substitution polymerizations can be used to form polymers including primary amine groups, which can then be used in formation of the above depicted PG groups. Many bisphenol compounds having at least one primary amine group thereon are available for formation of suitable polymeric materials via this route. Alternatively, some polymeric materials may be functionalized after polymerization to incorporate primary amine groups that then may be used in the formation of the above depicted PG groups.

Referring now to FIG. 1, an exemplary synthetic scheme for preparing a 1,3,5-hexahydrotriazine functionalized monomer and a 1,3,5-hexahydrotriazine functionalized polymer is depicted. A starting material **10** includes a polymerizable group **20**, a body group **30** connected to the polymerizable group **20**, and a primary amine moiety **40** connected to the body group **30**. Starting material **10** is reacted with a primary amine (R—NH₂) (a first primary amine compound) and paraformaldehyde ((CH₂O)_n) to form 1,3,5-hexahydrotriazine functionalized monomer **50**. 1,3,5-hexahydrotriazine functionalized monomer **50** maintains the polymerizable group **20** and body group **30** from the starting material **10**, however the primary amine moiety **40** reacts with primary amine (R—NH₂) and paraformaldehyde ((CH₂O)_n) to form 1,3,5-hexahydrotriazine moiety **60** as depicted. The "R" group of the primary amine (R—NH₂) is not specifically limited according to the present disclosure, but in this example "R" includes at least one carbon atom. The 1,3,5-hexahydrotriazine moiety **60** is linked to two "R" groups from the primary amine(s)—one at each of the nitrogen atoms at the nominal "3" and "5" positions of the triazine ring. The nitrogen atom at the nominal "1" position of the triazine ring is bonded to body group **30**. The respective "R" groups linked to "3" and "5" nitrogen atoms in the 1,3,5-hexahydrotriazine moiety **60** do not necessarily have the same chemical structure and may be different from each other if, for example, a mixture of different primary amine compounds is provided in the reaction mixture.

The primary amine (R—NH₂) reacted with starting material **10** can be, without limitation, (3-aminopropyl)triethoxysilane (APTES), methylamine (CH₃NH₂), a primary amine substituted alkyl chain such as 1-ethylamine (CH₃CH₂NH₂), 1-propylamine (CH₃CH₂CH₂NH₂), or longer alkyl chains of generalized formula (CH₃(CH₂)_nNH₂), benzylamine (1-phenylmethanamine) (C₆H₅CH₂NH₂), isopropylamine (propan-2-

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amine) $((\text{CH}_3)_2\text{CH}_2\text{NH}_2)$ or branched alkyl chains with at least one primary amine functional group substituted thereon. The primary amine ($\text{R}-\text{NH}_2$) may also be a mixture of two or more primary amines of different structures.

1,3,5-hexahydrotriazine functionalized monomer **50** can be polymerized (via reaction of polymerizable group **20**) to form 1,3,5-hexahydrotriazine functionalized polymer **70**. 1,3,5-hexahydrotriazine functionalized polymer **70** has a polymeric backbone **80** and, as depicted in FIG. 1, pendant 1,3,5-hexahydrotriazine moiety **60** groups (via body group **30**) on each of “n” repeat units. The number of repeat units (“n”) (i.e., the degree of polymerization) of a 1,3,5-hexahydrotriazine functionalized polymer **70** is not specifically limited and may be any number accessible by the selected polymerization method. For example, a free radical initiated polymerization method may result in a polymeric material having a few hundred to several thousand repeat units on average. And while each individual molecule of 1,3,5-hexahydrotriazine functionalized polymer **70** has a specific, integer value of “n,” 1,3,5-hexahydrotriazine functionalized polymer **70** as a material (as compared to an individual molecule of a material) will generally have a distribution of different “n” values rather than a single “n” value.

The polymerization of 1,3,5-hexahydrotriazine functionalized monomer **50** may be performed by any available technique, for example, and without limitation, the polymerization method can be radical-initiated or anionic-catalyzed solution phase polymerization, emulsion polymerization, suspension polymerization. The polymerization technique may be used to generate a polymer network, a star polymer, a copolymer, or a hyper-branched polymer according to the selected reaction conditions and methods.

While 1,3,5-hexahydrotriazine functionalized polymer **70** is depicted in FIG. 1 as a homopolymer (i.e., one type of repeat unit only), it is understood by those of ordinary skill in the art that other repeat unit types can be included in 1,3,5-hexahydrotriazine functionalized polymer **70**. For example, inclusion of other monomeric materials having a polymerizable group similar to or the same as polymerizable group **20**, it is possible to provide copolymers incorporating 1,3,5-hexahydrotriazine functionalized monomer **50** as one of at least two repeating groups. As a specific example, 1,3,5-hexahydrotriazine functionalized monomer **50** could be polymerized in the presence of styrene monomer to generate a copolymer including both styrene repeat units and 1,3,5-hexahydrotriazine functionalized repeat units.

A copolymer incorporating repeat units corresponding in structure to 1,3,5-hexahydrotriazine functionalized polymer **70** can be a random copolymer, alternating copolymer, periodic copolymer, statistical copolymer, and/or a block copolymer according to the selected copolymerization method and the selected co-monomer(s). Additionally, the number of different types of repeating units in a copolymer is not limited to two, but may also be three or more types.

As known in the art, depending on selected polymerization method, 1,3,5-hexahydrotriazine functionalized polymer **70** may also incorporate various end-chain groups (“end groups”) that are not specifically depicted in FIG. 1, but which are understood to be present according to the polymerization method used in forming the 1,3,5-hexahydrotriazine functionalized polymer **70**.

Polymerizable group **20** is depicted as a vinyl moiety on a phenyl ring type body group **30**. However, this is a specific example presented for purposes of explanation only. Polymerizable group **20** is not limited to a vinyl moiety directly linked to a phenyl ring (that is, polymerizable group **20** and body group **30** do not have to collectively form a styrenyl

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group). For example, starting material **10** can be a primary amine functionalized methacrylate material. In other examples, starting material **10** can be a primary amine functionalized aromatic diol-type monomer or a primary amine functionalized bisphenol-type monomer that could be polymerized via nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$) reaction with a material such as, for example, 1-fluoro-4-(4-fluorobenzenesulfonyl)benzene.

FIG. 2 depicts an exemplary synthetic scheme for preparing a 1,3,5-hexahydrotriazine functionalized polymer. When compared to FIG. 1, FIG. 2 depicts a route from starting material **10** to 1,3,5-hexahydrotriazine functionalized polymer **70** that does not proceed through the 1,3,5-hexahydrotriazine functionalized monomer **50**. Rather, according to the scheme of FIG. 2, the starting material **10** is first polymerized to primary amine functionalized polymer **90**, which is then reacted with a primary amine ($\text{R}-\text{NH}_2$) and paraformaldehyde $((\text{CH}_2\text{O})_n)$ to form 1,3,5-hexahydrotriazine functionalized polymer **70**. The 1,3,5-hexahydrotriazine functionalized polymers **70** prepared according to FIG. 1 and FIG. 2 are substantially similar and the primary amine ($\text{R}-\text{NH}_2$) used in the scheme depicted in FIG. 2 is as described above with respect to the scheme depicted in FIG. 1. While primary amine functionalized polymer **90** is depicted as a homopolymer in FIG. 2, it may also be copolymer having two or more different types of repeat units.

A potential advantage of the scheme of FIG. 2 is the polymerization method and conditions used to form primary amine functionalized polymer **90** may be selected without regard to the presence of 1,3,5-hexahydrotriazine moiety **60** and the “R” groups attached thereto. For example, the intended “R” groups in the final product 1,3,5-hexahydrotriazine functionalized polymer **70** may include moieties which are susceptible to reactions with radicals or other catalysts used in the formation of primary amine functionalized polymer **90**. For example, the “R” group may include alkyne or alkene functionalities. The synthesis of primary amine functionalized polymer **90** could also include exposure to acids, which would react with a 1,3,5-hexahydrotriazine moiety **60** if it was present.

The synthetic route to primary amine functionalized polymer **90** is depicted in FIG. 2 as a single step from starting material **10**; however synthesis of polymer **90** may be more complex. For example, primary amine functionalized polymer **90** could be a portion of a graft polymer, a comb polymer, a block copolymer, a star polymer, a hyper-branched polymer, or the like requiring a multiple step synthetic process. Also, because primary amine functionalized polymer **90** is separately synthesized, it can be “pre-processed” before the reaction step used for forming 1,3,5-hexahydrotriazine functionalized polymer **70**. For example, primary amine functionalized polymer **90** can be sorted/filtered by molecular weight and/or purified by existing techniques after it is synthesized and before forming 1,3,5-hexahydrotriazine functionalized polymer **70**.

FIG. 3 depicts an exemplary synthetic scheme for preparing a chemically reversing crosslinked polymer material. When compared to FIG. 2, FIG. 3 depicts a route to a crosslinked polymer **100** from starting material **10** through a primary amine functionalized polymer **90**. The initial polymerization step from starting material **10** to polymer **90** is the same as depicted in FIG. 2; however, instead of reacting polymer **90** with an additional primary amine ($\text{R}-\text{NH}_2$), only paraformaldehyde $((\text{CH}_2\text{O})_n)$ is specifically provided to the reaction mixture. Thus, in effect, the primary amine group **40** on polymer **90** serves as the additional primary amine ($\text{R}-\text{NH}_2$) in the scheme, and the resulting crosslinked poly-

mer **100** includes a 1,3,5-hexahydrotriazine moiety **60** linking three different body groups **30**, which in turn are linked to three polymerized groups **80**. The primary amine groups **40** serving as the primary amine ($R-NH_2$) may be located on different polymer chains or may be different repeat units within the same polymer chain. In such situations, the "R" group of the primary amine ($R-NH_2$) includes a body group **30** and a polymerized group **80** along with the other repeat units connected thereto.

In general, all other things being equal, a crosslinked material has improved mechanical strength and thermal stability as compared to the non-crosslinked material. But crosslinked materials are typically difficult to remove, recycle, or reprocess. However, the 1,3,5-hexahydrotriazine moiety **60** is chemically reversible to its precursor materials when exposed to acid. Thus, crosslinked polymer **100** can be reverted to its precursors (primary amine functionalized polymer **90** and paraformaldehyde) upon exposure to acid. Thus, crosslinked polymer **100** can be "de-crosslinked" and thus becomes removable, recyclable, and reprocessible even after being cured/set. For example, while crosslinked polymer **100** would generally (assuming a significant crosslink density) be insoluble in common solvents, primary amine functionalized polymer **90** can be selected so as to be soluble in various common solvents.

A crosslinked material incorporating 1,3,5-hexahydrotriazine moiety **60** can also be reformed (re-crosslinked) after breakdown by subsequently exposing the de-crosslinked material to paraformaldehyde. Thus, materials incorporating 1,3,5-hexahydrotriazine moiety **60** based crosslinks can be de-crosslinked and re-crosslinked on demand. This type of chemically reversible crosslinking provides access to polymeric materials with the ability to be reworked, healed, reprocessed, and/or removed as required.

In a particular embodiment, crosslinked polymer **100** can be a bead for use as chromatographic packing material. For example, crosslinked polymer **100** can be a crosslinked polystyrene bead.

FIG. 4 depicts an exemplary synthetic scheme for preparing a chemically reversing crosslinkable monomeric material. While FIG. 3 depicts a scheme for preparing a chemically reversible crosslinked resin from a primary amine functionalized polymer **90**, an alternative method for forming a chemically reversible crosslinked resin would be to polymerize a chemically reversing crosslinkable monomer **110** with other types of monomer material, for example styrene monomer. Alternatively, monomer **110** could be self-polymerized without addition of other monomer types.

In a particular embodiment, crosslinkable monomer **110** can be polymerized along with styrene to form a crosslinked polystyrene bead for use as chromatographic packing material as an example. Such crosslinked beads may be formed using suspension or emulsion polymerization techniques to provide controlled bead sizes. The presence of 1,3,5-hexahydrotriazine moiety **60** in the crosslinked beads would allow for "de-crosslinking" upon exposure to acids such that the initially crosslinked beads could subsequently be dissolved by solvents for removal, recycling, or reprocessing. 1,3,5-hexahydrotriazine moiety **60**, as will be discussed further below, can be converted to other functional groups such as thioether and a dithiazine. These groups in turn can be reacted to form various other functional groups allowing the beads to be processed to include a variety of different functional groups.

FIG. 5 depicts an exemplary synthetic scheme for preparing a dithiazine functionalized polymer from a 1,3,5-hexahydrotriazine functionalized polymer. A 1,3,5-hexahydrotriazine

functionalized polymer **70**, prepared as described in association with FIG. 1 or FIG. 2, for example, is reacted with hydrogen sulfide (H_2S) to form dithiazine functionalized polymer **120**. When exposed to H_2S , 1,3,5-hexahydrotriazine moiety **60** converts to dithiazine moiety **130**, consequently 1,3,5-hexahydrotriazine functionalized polymer **70** converts to dithiazine functionalized polymer **120** upon exposure to H_2S . Such H_2S exposure may be for purposes of forming the dithiazine functionalized polymer **120** for a subsequent use, or may occur during the use of 1,3,5-hexahydrotriazine functionalized polymer **70** as a sulfur-scavenging material when, for example, 1,3,5-hexahydrotriazine functionalized polymer **70** is included in a oil or natural gas storage tank or pipeline as a coating, an additive, or a filtration medium. In some embodiments, the filtration medium may comprise crosslinked beads formed via suspension or emulsion polymerization techniques. In various embodiments, the filtration medium can be packed into a column, coated on a substrate, or formed into a fabric or mesh.

FIG. 6 depicts an exemplary synthetic scheme for preparing a thioether functionalized polymer from a 1,3,5-hexahydrotriazine functionalized polymer. 1,3,5-hexahydrotriazine functionalized polymer **70**, prepared as described in association with FIG. 1 or FIG. 2, for example, is reacted with a thiol ($R-SH$) compound to form thioether functionalized polymer **140**. When exposed to a thiol, 1,3,5-hexahydrotriazine moiety **60** converts to thioether moiety **150**, consequently 1,3,5-hexahydrotriazine functionalized polymer **70** converts to thioether functionalized polymer **140** upon exposure to a thiol. Without limitation, the thiol ($R-SH$) compound can be thiophenol, methyl mercaptan (methanethiol), or ethyl mercaptan (ethanethiol).

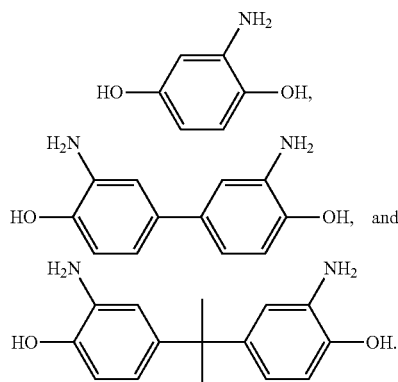
FIG. 7 depicts an exemplary synthetic scheme for preparing a 1,3,5-hexahydrotriazine functionalized polymer from an amino-substituted aromatic diol-type monomer. In the depicted scheme, starting material **160** is polymerized with starting material **165** in the presence of, for example, potassium carbonate (K_2CO_3) and a solvent (such as N-methyl-2-pyrrolidone (NMP)) to form a primary amine substituted polymer **170** via, for example, a nucleophilic aromatic substitution reaction. Primary amine substituted polymer **170** is conceptually similar to primary amine functionalized polymer **90** and may be consider a specific example of primary amine functionalized polymer **90** having a structure in which body groups **30** and polymerized groups **80** are structurally the same components rather than distinct components as depicted in FIG. 2, for example. Primary amine functionalized polymer **170** can be isolated/purified and then may be reacted with a primary amine ($R-NH_2$) and paraformaldehyde ($(CH_2O)_n$) to form 1,3,5-hexahydrotriazine functionalized polymer **180**. In some embodiments, it may be preferable to react primary amine functionalized polymer **170** with the primary amine ($R-NH_2$) and paraformaldehyde at relatively low temperatures, such as at or below approximately $50^\circ C$. to avoid unwanted side reactions.

1,3,5-hexahydrotriazine functionalized polymer **180** is conceptually similar to 1,3,5-hexahydrotriazine functionalized polymer **70** described above. As such, 1,3,5-hexahydrotriazine functionalized polymer **180** may also be reacted according to the schemes depicted in FIG. 5 and FIG. 6 to form corresponding dithiazine functionalized polymers and thioether functionalized polymers, respectively.

While starting material **160** in FIG. 7 is depicted as 2-aminobenzene-1,4-diol, this is a specific example for purposes of explanation only. In general, starting material **160** may be an aromatic diol-type monomer including at least one primary amine substituted aromatic ring or a bisphenol monomer

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including at least one primary amine substituted aromatic ring. For example, starting material **160** may be selected from a group of compounds including the following:



Starting material **165** is specifically depicted as 1-fluoro-4-(4-fluorobenzenesulfonyl)benzene. However, this is a specific example provided for purposes of explanation only and starting material **165** is not limited to this material. For example, other leaving groups besides fluorine (fluoride ion) could be included in starting material **165**. Other halides or tosylate (TsO^-) ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$) could be adopted as the leaving groups in starting material **165**. In general, starting material **165** should have at least two accessible leaving groups (e.g., fluoride ions) bonded to aromatic rings so polymerization with starting material **160** (or starting material **190** (see FIG. 8)) may occur via, for example, nucleophilic aromatic substitution reactions. Reaction between starting material **160** and starting material **165** is, in general, promoted by the presence of an electron withdrawing group on the aromatic ring to which the leaving group is attached. Starting material **165** is depicted in FIG. 7 with a sulfonyl group ($-\text{SO}_2-$) as the electron withdrawing group, though other electron withdrawing groups may be incorporated instead of or in addition to the sulfonyl group. Thus, as an example scheme, starting material **160** and starting material **165** can be polymerized with each other to form an amino-substituted polysulfone via nucleophilic aromatic substitution. The amino-substituted polysulfone may then be subsequently reacted with a primary amine ($\text{R}-\text{NH}_2$) and paraformaldehyde ($(\text{CH}_2\text{O})_n$) to provide a polymeric material having a pendant 1,3,5 hexahydrotriazine moiety. It may be preferable to isolate or purify the amino-substituted polymer (e.g., polymer **170**) before reacting it with the primary amine ($\text{R}-\text{NH}_2$) and paraformaldehyde ($(\text{CH}_2\text{O})_n$).

In some embodiments, when two or more primary amine functional groups are present in starting material **160**, the corresponding 1,3,5-hexahydrotriazine functionalized polymer **180** formed from the starting material **160** may have two or more 1,3,5-hexahydrotriazine moieties and, as such, the corresponding 1,3,5-hexahydrotriazine functionalized polymer **180** may have a repeat unit including two or more 1,3,5-hexahydrotriazine moieties.

In addition, starting material **160** may in some embodiments be processed similarly to starting material **10** as depicted in FIG. 4 to form a material conceptually similar to chemically reversing crosslinkable monomer **110**. That is, for example, to form a material such as starting material **190** (see FIG. 8) wherein each R group of starting material **190** is a hydroquinone moiety. In forming a material similar to chemically reversing crosslinkable monomer **110** from starting

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material **160**, it may be necessary to protect the phenol-type ($-\text{OH}$) moieties of starting material **160** before the starting material **160** is exposed to paraformaldehyde ($(\text{CH}_2\text{O})_n$).

FIG. 8 depicts an exemplary synthetic scheme for preparing a 1,3,5-hexahydrotriazine functionalized polymer from a 1,3,5-hexahydrotriazine-substituted aromatic diol-type monomer. In FIG. 8, starting material **190** is reacted with starting material **165** in the presence of in the presence of potassium carbonate (K_2CO_3) and a solvent (such as N-methyl-2-pyrrolidone (NMP)) to form 1,3,5-hexahydrotriazine functionalized polymer **180**.

As depicted in FIG. 8, starting material **190** is a 1,3,5-hexahydrotriazine functionalized aromatic diol-type monomer and starting material **165** is the same as described with respect to FIG. 7. In general, starting material **190** is not limited to specific structure depicted in FIG. 8, but may be any one of a 1,3,5-hexahydrotriazine functionalized aromatic diol-type monomer or a 1,3,5-hexahydrotriazine functionalized bisphenol-type monomer. For example, starting material **190** can be prepared by reaction of starting material **160** with a primary amine ($\text{R}-\text{NH}_2$) and paraformaldehyde ($(\text{CH}_2\text{O})_n$) according to a reaction scheme conceptually similar to the reaction of starting material **10** to form 1,3,5-hexahydrotriazine functionalized monomer **50**, as described with respect to FIG. 1; however, synthesis of starting material **190** may require first protecting the phenol-type ($-\text{OH}$) moieties of starting material **160** before the starting material **160** is exposed to paraformaldehyde ($(\text{CH}_2\text{O})_n$). In some embodiments, it may be possible to use a protected version of starting material **190** (that is, starting material **190** with protecting groups still at the phenol-type ($-\text{OH}$) positions) directly in the polymerization reaction with starting material **165** since condensation reaction conditions (e.g., high temperatures) may be selected that remove the protecting groups from the protected version of starting material **190**, effectively making (unprotected) starting material **190** available for reaction with starting material **165**.

In some embodiments, when two or more primary amine functional groups are present in starting material **160**, the corresponding starting material **190** formed from starting material **160** may have two or more 1,3,5-hexahydrotriazine moieties and, as such, the corresponding 1,3,5-hexahydrotriazine functionalized polymer **180** may have a repeat unit including two or more 1,3,5-hexahydrotriazine moieties.

"R" as used in the above descriptions of chemical structures refers to a radical unit including at least one carbon atom. "R" may be the same or different in each instance of use within a chemical structure. That is, two or more "R" groups depicted in a single chemical structure are not necessarily the same radical unit, though they may be the same in some embodiments. Additionally, "R" depicted in different chemical structures or compounds is not necessarily the same radical unit and may, in general, be independently selected. Without limitation, a radical unit depicted as "R" may include an alkyl group, an aryl group, a silane group, an alkyne group, an alkene group, an alcohol group, an epoxide group, an amine group, a cyanate group, a carboxylic acid group, an ester group, a phenolic group, and/or a succinimide group. In specific embodiments, the radical unit depicted as "R" may be a methyl group, a methanol group, a primary amine substituted alkyl group, a tertiary amine substituted alkyl group, or a triethoxysilane group. In some embodiments, "R" may represent a portion of a polymeric or oligomeric chain.

In general, in this specification and accompanying figures, when a molecular structure includes a repeating group designated as repeating for "n" units, this designation indicates that the material is polymeric or oligomeric rather than that

"n" has a specific numerical value and the different instances of "n" within formulas or figures are not required to have the same numerical value. Furthermore, polymeric and oligomeric materials (as compared to a single molecule of a polymeric or oligomeric material) may have a distribution of chain lengths ("n" values) rather than a single chain length ("n" value). Thus, when referring to polymeric or oligomeric materials rather than an individual molecule of such materials, "n" need not be a specific numerical value or even an integer value, but rather may correspond to some averaged value for the distribution of the degree of polymerization for molecules within the material. The specific distribution of "n" values is generally determined by the details (e.g., relative amount of initiator to monomer, temperature, reaction times, method of polymerization, etc.) of the process used in forming the polymeric or oligomeric material, but materials may also subsequently be processed (e.g., sorted/separated by size after synthesis) to alter the distribution of "n" values. Similarly, in this specification and accompanying figures, within molecular formulas that include different repeating groups (e.g., as in crosslinked polymer 100), each of the different repeating groups may be designated as repeating for "n" units; however, in this context, this does not imply each of the different repeating groups within the molecular formula repeats for the same specific "n" value (though without limitation these "n" values may also be the same). In general, the value of "n" for any specific molecule of a polymeric material may be any number that is accessible by at least one polymerization method and the value of "n" is not otherwise limited. For example, in some embodiments, "n" for a specific molecule may be any number greater than one (1) and less than or equal to about three hundred (300). In other embodiments, "n" for a specific molecule may be any number greater than or equal to about ten (10) and less than or equal to about one hundred (100). In some embodiments, when a 1,3,5-hexahydrothiazine, dithiazine, or thioether monomer group is included in a copolymer, the value of "n" associated with such a monomer group may be equal to or greater than one (1) and less than or equal to about three hundred (300). In other embodiments, when a 1,3,5-hexahydrothiazine, dithiazine, or thioether monomer group is included in a copolymer, the value of "n" associated with such a monomer group may be equal to or greater than about ten (10) and less than or equal to about one hundred (100).

The descriptions of the various example embodiments have been presented for purposes of illustration, and are not intended to be exhaustive representations of the present disclosure. Many modifications and variations will be apparent to those of ordinary skill in the art without departing from the scope of the present disclosure. The terminology used herein was chosen to best explain the principles of the various embodiments, the practical application or technical improvement over technologies found in the marketplace, or to enable others of ordinary skill in the art to understand the embodiments disclosed herein.

While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the scope of

the present disclosure, and the scope of the present disclosure is determined by the claims that follow.

What is claimed is:

1. A method, comprising:
 - exposing a first monomer including a primary amine functional group to paraformaldehyde and a first primary amine compound and forming a second monomer including a 1,3,5-hexahydrothiazine group; and
 - polymerizing the second monomer and forming a first polymer including the 1,3,5-hexahydrothiazine group.
2. The method of claim 1, further comprising: exposing the first polymer to hydrogen sulfide.
3. The method of claim 1, further comprising: exposing the first polymer to a thiol compound.
4. The method of claim 1, wherein the first monomer is one of an amino-substituted styrene, an amino-substituted bisphenol, an amino-substituted aromatic diol, and an amino-substituted methacrylate.
5. The method of claim 1, wherein polymerizing the second monomer and forming the first polymer includes a radical initiated polymerization.
6. The method of claim 1, wherein the first primary amine compound has the same chemical structure as the first monomer.
7. The method of claim 1, wherein the 1,3,5-hexahydrothiazine group is pendant on the first polymer.
8. The method of claim 1, wherein the 1,3,5-hexahydrothiazine group is part of a crosslink in the first polymer.
9. The method of claim 1, wherein the first polymer is a copolymer of the second monomer and a third monomer.
10. The method of claim 9, wherein the third monomer is styrene.
11. The method of claim 1, further comprising: exposing the first polymer to acid and forming a second polymer including a primary amine functional group.
12. A method, comprising:
 - polymerizing a first monomer including a primary amine functional group and forming a first polymer including the primary amine functional group; and
 - exposing the first polymer to paraformaldehyde and a first primary amine compound and forming a second polymer including a 1,3,5-hexahydrothiazine group.
13. The method of claim 12, wherein the first primary amine compound has the same chemical structure as the first polymer.
14. The method of claim 12, further comprising: exposing the second polymer to hydrogen sulfide or a thiol compound.
15. The method of claim 12, wherein the first monomer is one of an amino-substituted styrene, an amino-substituted bisphenol, an amino-substituted aromatic diol, and an amino-substituted methacrylate.
16. The method of claim 12, wherein the first polymer is one of a block copolymer, a star polymer, a comb polymer, and a hyperbranched polymer.
17. The method of claim 12, further comprising: exposing the second polymer to acid and re-forming the first polymer.

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